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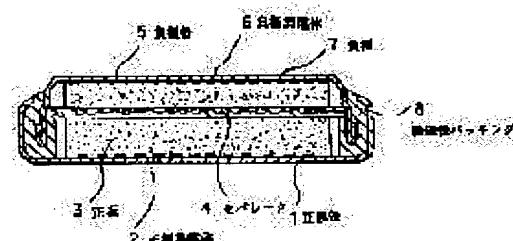
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(54) MANUFACTURE OF NEGATIVE ELECTRODE FOR LITHIUM SECONDARY BATTERY, AND LITHIUM SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a method for manufacturing a more practical negative electrode for lithium secondary battery with high capacity and low degree of storage deterioration, and a lithium secondary battery having this negative electrode.

CONSTITUTION: A metal foil consisting of metal lithium or lithium-aluminum alloy which constitutes a negative electrode is left under an argon gas atmosphere containing a small amount of hydrogen fluoride or hydrogen chloride to form a lithium fluoride film or lithium chloride film on the metal foil surface. A lithium secondary battery has a positive electrode 3, a negative electrode 7 having lithium or lithium-aluminum alloy as negative electrode active material, and a lithium ion conductive electrolyte, and the negative electrode active material has a thin lithium fluoride or lithium chloride film and also a hydrogen fluoride or hydrogen chloride film 100-1000nm in thickness formed on the surface.



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CLAIMS

[Claim(s)]

[Claim 1] A manufacture method of a negative electrode for lithium secondary batteries characterized by leaving a metallic foil which consists of a metal lithium or lithium-aluminum alloy under argon gas containing a small amount of thin FUTSU hydrogen or thin hydrogen chloride, or nitrogen-gas-atmosphere mind, and making a lithium fluoride film or a lithium-chloride film form in said metallic foil surface.

[Claim 2] It is the lithium secondary battery characterized by being the lithium secondary battery which possesses a positive electrode, a negative electrode equipped with a metal lithium or lithium-aluminum alloy as negative-electrode active materials, and the lithium ion conductivity electrolytic solution, and changes, and said negative-electrode active material having thin lithium fluoride or a lithium-chloride film on the surface.

[Claim 3] Setting a positive electrode, a negative electrode equipped with a metal lithium or lithium-aluminum alloy as negative-electrode active materials, and the lithium ion conductivity electrolytic solution to a lithium secondary battery which possesses and changes, said negative-electrode active material is thickness to the surface. A lithium secondary battery characterized by forming 100-1000nm lithium fluoride or a lithium-chloride film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the lithium secondary battery aiming at evasion of the manufacture method of the negative electrode for lithium secondary batteries, high-capacity-izing, and storage deterioration.

[0002]

[Description of the Prior Art] In recent years, the lithium secondary battery which uses a lithium as a negative-electrode active material attracts attention as a high energy density cell as a nonaqueous electrolyte cell. That is, the lithium primary-cell nature which uses manganese-dioxide (MnO₂) and Carbon n fluoride (CF₂), a thionyl chloride (SOCl₂), etc. as positive active material, and changes is used abundantly as a calculator and a backup cell of power supply 7 memory of a clock. On the other hand, the alkali rechargeable battery represented by a nickel-hydrogen rechargeable battery or the nickel-cadmium rechargeable battery is widely put in practical use as an actuation power supply of various kinds of device systems, such as for example, a portable telephone set and a pocket mold image pick-up machine. And since this kind of rechargeable battery repeats reservation of the power by charge actuation thru/or storage, and the drive (discharge) of the load which used as the power supply said power secured thru/or stored and can perform them, it is incorporated and used for said various kinds of device systems.

[0003] Moreover, about these rechargeable batteries, with the miniaturization of said portable telephone set, a pocket mold image pick-up machine, etc., and lightweight-izing, the rechargeable battery of high energy density is demanded as a power supply, and development of the lithium secondary battery which uses a lithium as a negative-electrode active material corresponding to this demand is furthered.

[0004] By the way, generally with a lithium secondary battery, it is, as a (a) negative-electrode active material, a lithium They are propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, and gamma as the (b) lithium conductivity electrolytic solution. In non-aqueous solvents, such as - butyrolactone and a tetrahydrofuran for example, - LiClO₄, LiBF₄, LiAsF₆, and LiPF₆ etc. -- the nonaqueous electrolyte which is made to dissolve lithium salt and changes -- Or a lithium ion conductivity solid electrolyte (c) The compound which participates in a topochemical reaction among lithiums, such as a titanium sulfide, a molybdenum sulfide, a banazin san ghost, a cobalt oxide, and a manganic acid ghost, is mainly further used as positive active material, respectively.

[0005]

[Problem(s) to be Solved by the Invention] However, in the lithium secondary battery known conventionally, the count (charge-and-discharge cycle) life of charge and discharge also has the problem of being short, low [charge-and-discharge effectiveness]. And it is thought that this cause has the large place undertaken to deterioration of the lithium by the reaction of a negative-electrode active material lithium and nonaqueous electrolyte. That is, in case the lithium which dissolved into nonaqueous electrolyte as a lithium ion at the time of discharge deposits at the time of charge, it reacts with a solvent, for example, lithium fluoride, a lithium chloride, etc. generate it. And if the repeat of charge and discharge progresses, from the portion generated [lithium chloride / said / lithium fluoride, lithium chloride, etc.], a dent light-like (arborescence) lithium or a corpuscle-like lithium deposits, and the cycle life of a lifting and charge and discharge is shortened for the internal short circuit.

[0006] In addition, the cause of generation and a deposit of the lithium of the shape of said shape of a dent light and a corpuscle is considered like the next. That is, when the surface of a metal lithium or a lithium-aluminum alloy was covered with the coat of lithium oxide or a lithium hydroxide, it assembles on a cell and it is generally charged as it was, it is a solute in the electrolytic solution. A part decomposes into LiClO₄ and LiPF₆, lithium fluoride and a lithium chloride generate, and it is easy to deposit on the coat of said lithium oxide and lithium hydroxide partially (into especially, surface muscle-like portion). And although lithium oxide and the lithium hydroxide which have constituted the substrate will disappear if it discharges in this condition, lithium fluoride and a lithium chloride remain as it is, and it is thought that are the repeat of charge and discharge, and lithium fluoride and a lithium chloride continue depositing in said extant lithium fluoride and extant lithium-chloride side alternatively, it deposits on them, a deposit of the

lithium of the shape of the shape of a dent light and a corpuscle becomes easy to take place, and a separator is broken through. Moreover, since electrolytic concentration decreases in order for a part of solute in said electrolytic solution to decompose with a deposit of the lithium of the shape of this shape of a dent light and a corpuscle, charge-and-discharge effectiveness will also fall.

[0007] To use occlusion and the carbonaceous material which can be emitted is also tried in the lithium as a negative electrode built into a lithium secondary battery to the problem of said charge-and-discharge cycle life etc. That is, preventing the reaction of said lithium and nonaqueous electrolyte and deterioration of the negative electrode by deposit of a dent light is proposed by incorporating the negative electrode of a configuration of having made corks, the resin sintered compact, the carbon fiber, the pyrolysis vapor growth carbon body, etc. support a lithium (negative-electrode active material). And although deterioration of said negative electrode etc. can be prevented by taking such a configuration, on the other hand compared with the rechargeable battery at the time of using a metal lithium as a negative electrode as it was, there is a problem that the degree of storage deterioration is also large, low [charge-and-discharge capacity].

[0008] this invention person copes with the deposit problem of the lithium of the shape of said shape of a dent light, and a corpuscle. If the thin lithium fluoride film or the lithium-chloride film is made to form in the surface of the metal lithium which accomplishes a negative-electrode active material, or a lithium-aluminum alloy beforehand in advance of the assembly of a cell as a result of advancing examination variously The reaction of the solute in the electrolytic solution by charge and a negative-electrode active material was controlled, and it found out that a local deposit of lithium fluoride and a lithium chloride was reduced.

[0009] It was made based on such knowledge, and this invention is high capacity, and its degree of storage deterioration is also low and it aims at offer of the lithium secondary battery possessing the manufacture method of the negative electrode for lithium secondary batteries with more high practicality, and this negative electrode.

[0010]

[Means for Solving the Problem] A manufacture method of a negative electrode for lithium secondary batteries concerning this invention leaves a metallic foil which consists of a metal lithium or lithium-aluminum alloy under argon gas containing a small amount of FUTSU hydrogen or hydrogen chloride, or nitrogen-gas-atmosphere mind, and is characterized by making a FUTSU hydrogen film or a hydrogen chloride film form in said metallic foil surface.

[0011] A lithium secondary battery concerning this invention is a lithium secondary battery which possesses a positive electrode, a negative electrode equipped with a metal lithium or lithium-aluminum alloy as negative-electrode active materials, and the lithium ion conductivity electrolytic solution, and changes, and lithium fluoride or a lithium-chloride film thin on the surface is [said negative-electrode active material] still more specifically thickness. It is characterized by forming 100-1000nm lithium fluoride or a lithium-chloride film.

[0012] As mentioned above, a manufacture method of a negative electrode for lithium secondary batteries concerning this invention and a lithium secondary battery which possesses this negative electrode and changes make it a main point to cover the surface of a negative-electrode active material with a thin lithium fluoride film or a lithium-chloride film. Here, thickness of a lithium fluoride film or a lithium-chloride film is in a general target, although based on capacity of a lithium secondary battery, magnitude, etc. About 100-1000nm is desirable. That is, thickness of a covering film It is because reinforcement is inferior, orientation to be easy to exfoliate from a negative-electrode active material side is accepted, and orientation which electric resistance increases, and internal resistance of a cell increases as a result, and has a bad influence on discharge effectiveness will be accepted in less than 100nm if it exceeds 1000nm.

[0013] The above and a negative electrode for lithium secondary batteries concerning this invention are for example, capacity concentration about a metallic foil which consists of a metal lithium or lithium-aluminum alloy which accomplishes a negative-electrode active material. A lithium fluoride film or a lithium-chloride film of request thickness can be formed in said metallic foil surface by leaving it under argon gas containing about 0.005 - 0.05% of a small amount of FUTSU hydrogen or hydrogen chloride, or nitrogen-gas-atmosphere mind. Here, neglect time amount of a negative-electrode active material is at a room temperature, when it considers as 0.01 - 0.03% of said capacity concentration, although influenced by concentration, temperature, etc. of FUTSU hydrogen in an ambient atmosphere, or a hydrogen chloride. It is setting it as a 30 - 40-minute about room at 40 degrees C for about 1 to 2 hours, and all-out almost uniform thin lithium fluoride film or thin lithium-chloride film can be covered and formed easily and certainly.

[0014] a lithium secondary battery concerning this invention -- it is and chalcogen compounds, such as oxides, such as amorphous vanadium pentoxide which contains a lithium manganese multiple oxide, a manganese dioxide, a lithium content nickel oxide, a lithium content cobalt oxide, a lithium content nickel cobalt oxide, and a lithium, for example, 2 titanium sulfides, and molybdenum disulfide, etc. are mentioned as the quality of the material which accomplishes a positive electrode.

[0015] moreover, as the lithium ion conductivity electrolytic solution which can be used in this invention For example,

ethylene carbonate, propylene carbonate, butylene carbonate, gamma - A butyrolactone, a sulfolane, an acetonitrile, 1, 2-dimethoxymethane, 1, 3-dimethoxypropane, wood ether, a tetrahydrofuran, To a non-aqueous solvent which consists of at least one sort chosen from a herd of 2-methyl tetrahydrofuran, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate Lithium perchlorate (LiClO₄), a 6 phosphorus-fluoride acid lithium (LiPF₆), Hoe lithium fluoride (LiBF₄), a 6 arsenic-fluoride lithium (LiAsF₆), Lithium salt, such as a trifluoro methansulfonic acid lithium (LiCF₃ SO₃) (electrolyte) 0.5 - 1.5 mol/l Generally nonaqueous electrolyte which carried out degree dissolution is mentioned. In addition, a solid electrolyte of lithium ion conductivity, for example, a solid polymer electrolyte which made a high molecular compound compound lithium salt, can also be used instead of said nonaqueous electrolyte.

[0016] Furthermore, as a separator which carries out insulating isolation of between a negative electrode and a positive electrode, nonwoven fabrics, porous films, etc. of polyolefine system resin, such as polyethylene and polypropylene, can be used, for example. And while this separator carries out a role of said inter-electrode insulating elongation, it functions also as support or a supporter of the lithium ion conductivity electrolytic solution.

[0017]

[Function] According to the manufacture method of the negative electrode for lithium secondary batteries concerning this invention, a thin lithium fluoride film almost uniform to a lithium system active substance side or a lithium-chloride film can be generated and formed easily. And since said generation, the fluoride to form, or a lithium-chloride film acts so that it may set at the time of charge and the reaction of the solute in the electrolytic solution and the negative-electrode active material itself may be prevented and controlled, while avoiding generation of a dent light etc. easily and presenting a high charge-and-discharge capacity, the negative electrode for lithium secondary batteries holding a good storage-proof property (there is little storage deterioration) is offered.

[0018] Moreover, since the negative electrode for lithium secondary batteries holding a good storage-proof property (there is little storage deterioration) was made to provide according to the built lithium secondary battery while presenting said high charge-and-discharge capacity, a storage-proof property is good and a high capacity RICHIU rechargeable battery is offered.

[0019]

[Example] With reference to drawing 1 , the example of this invention is explained below.

[0020] As creation place ** of an example 1 (A) positive electrode, and an active material, the powder of carbon black was prepared as a conductive material, and the powder of polytetrafluoroethylene was further prepared for the powder of vanadium pentoxide as a binder, respectively. Subsequently, said active material, the conductive material, and the binder were mixed and kneaded with the mass ratio at the rate of 90:10:5, and mixture was prepared. Then, a pressurization press machine is used and it is said mixture 2 ton/cm² Pressurization molding was carried out by the pressure and the positive electrode of a pellet type with a diameter [of 15mm] and a thickness of 0.77mm was created.

[0021] (B) Creation thickness of a negative electrode A 0.2mm lithium foil is prepared and it is about this lithium foil in the argon gas ambient atmosphere of hydrogen fluoride 0.01 capacity % content. 3-48hr neglect is carried out, the whole surface was covered and the lithium fluoride film with a thickness of 56-1200nm was made to generate and form. About the lithium foil (eight kinds) which made said lithium fluoride film generate and form, punching processing was carried out, respectively and the disc-like negative electrode with a diameter of 14mm was created. In addition, thickness measurement of said lithium fluoride film was performed by the electrochemistry quartz-resonator method.

[0022] (C) The non-aqueous-solvent rechargeable battery as a rechargeable battery assembles and shows an important section configuration to drawing 1 in cross section with an obligatory assembly means was assembled. First, it is 6 lithium fluoride to propylene carbonate after minding the positive-electrode charge collector 2 which changes from the extractives pan metal made from stainless steel with a diameter [of 12mm], and a thickness of 0.05mm to the inside of the positive-electrode can 1 which consists of stainless steel, containing and equipping with the positive electrode 3 of said created pellet type and laying a separator 4 on the positive electrode 3 of this pellet type further. The electrolytic solution prepared so that it might change with the concentration of 0.7 mols / l was poured in.

[0023] They are the diameter of 15mm, and thickness to the inside of the negative-electrode can 5 which similarly consists of stainless steel on the other hand. The negative-electrode charge collector 6 which consists of the 1.0mm extractives pan metal made from nickel was minded, and it contained and equipped with said created disc-like negative electrode 7. Then, the outer diameter of 20mm, thickness which equip opening of said positive-electrode can 1 with the insulating gasket 8, fit opening of the negative-electrode can 5 into opening of this positive-electrode can 1, caulk the positive-electrode can 1, seal said positive electrode 2, a separator 3, a negative electrode 7, etc., and change in the positive-electrode can 1 and the negative-electrode can 5 2.5mm coin form non-aqueous-solvent rechargeable battery Eight pieces were assembled.

[0024] Next, various kinds of characterization was performed about the non-aqueous-solvent rechargeable battery of

the above-mentioned configuration.

[0025] (D) each non-aqueous-solvent rechargeable battery after the spark test aforementioned assembly -- 250microA Constant current since a spark test is performed to 1.8 V -- further -- 250microA Constant current Charge to 3.4 V. it considers as 1 cycle -- the result of having carried out measurement evaluation is shown in a table 1 by making the ratio of the charge capacity in 100 cycle, and the capacity of 5 cycle eye into charge-and-discharge effectiveness.

[0026] The outsides which used the ***** lithium foil which it considers [foil] as a negative electrode and is not making the lithium fluoride film generate and form on the surface in the case of example of comparison 1 example 1 are the same conditions as the case of an example 1, and assembled the coin form non-aqueous-solvent rechargeable battery. Moreover, the result of having carried out measurement evaluation of the charge-and-discharge effectiveness on the same conditions as the case of an example 1 is collectively shown in a table 1 about this lithium secondary battery.

[0027]

表1

試料	放置時間	生成被膜 の厚さ(nm)	充放電効率 (%)
実施例1a	3	56	60
" 1b	6	77	77
" 1c	9	103	80
" 1d	12	250	84
" 1e	18	340	86
" 1f	24	600	80
" 1f	36	990	78
" 1g	48	1200	65
比較例1	—	—	60

The outside which left it in the argon ambient atmosphere containing a hydrogen chloride, generated and formed the lithium-chloride film, and created the negative electrode instead of in the case of example 2 example 1 leaving a metal lithium foil it being an argon ambient atmosphere containing hydrogen fluoride, and generating and forming a lithium fluoride film is the same conditioning as the case of an example 1, and is a coin form non-aqueous-solvent rechargeable battery. Eight pieces were assembled.

[0028] Moreover, the result of having performed various kinds of characterization on the same conditions as the case of an example 1 about this non-aqueous-solvent rechargeable battery is shown in a table 2.

[0029]

表2

試料	放置時間	生成被膜 の厚さ(nm)	充放電効率 (%)
実施例2a	3	80	76
" 2b	6	110	84
" 2c	9	200	87
" 2d	12	440	90
" 2e	18	680	88
" 2f	24	900	78
" 2f	36	1500	60
" 2g	48	2000	55

The outside which used the lithium aluminium alloy (lithium component 10 mass %) foil instead of using a metal lithium foil as material of a negative electrode in the case of example 3 example 1 is the same conditioning as the case of an example 1, and is a coin form non-aqueous-solvent rechargeable battery. Eight pieces were assembled.

[0030] Moreover, the result of having performed various kinds of characterization on the same conditions as the case of this likeness ***** of a non-aqueous-solvent rechargeable battery and an example 1 is shown in a table 3.

[0031] The outsides which used the ** lithium aluminium alloy foil which it considers [foil] as a negative electrode and is not making the lithium fluoride film generate and form on the surface in the case of example of comparison 2 example 1 are the same conditions as the case of an example 1, and assembled the coin form non-aqueous-solvent rechargeable battery. Moreover, the result of having carried out measurement evaluation of the charge-and-discharge

effectiveness on the same conditions as the case of an example 1 is collectively shown in a table 3 about this lithium secondary battery.

[0032]

表3

試料	放置時間	生成被膜 の厚さ (nm)	充放電効率 (%)
実施例3a	3	57	60
" 3b	6	80	77
" 3c	9	110	84
" 3d	12	240	86
" 3e	18	330	90
" 3f	24	580	85
" 3f	36	1000	78
" 3g	48	1300	65
比較例 2	—	—	71

The outside which used the lithium aluminium alloy (lithium component 10 mass %) foil instead of using a metal lithium foil as material of a negative electrode in the case of example 4 example 2 is the same conditioning as the case of an example 2, and is a coin form non-aqueous-solvent rechargeable battery. Eight pieces were assembled.

[0033] Moreover, the result of having performed various kinds of characterization on the same conditions as the case of this likeness ***** of a non-aqueous-solvent rechargeable battery and an example 1 is shown in a table 4.

[0034]

表4

試料	放置時間	生成被膜 の厚さ (nm)	充放電効率 (%)
実施例4a	3	82	71
" 4b	6	120	81
" 4c	9	190	88
" 4d	12	420	92
" 4e	18	660	85
" 4f	24	890	80
" 4f	36	1400	62
" 4g	48	1900	57

The negative electrode created by the manufacture method concerning this invention and the lithium secondary battery which made this negative electrode provide function as a power supply which is high capacity and was excellent in high charge-and-discharge effectiveness or keeping-proof so that the above-mentioned example and the example of a comparison may show.

[0035] In addition, this invention is not limited to the above-mentioned example, and can take various deformation in the range which does not deviate from the meaning of invention. For example, even if it takes the configuration which changed the constituent of a positive electrode, and the constituent of a separator into the positive electrode already known, the separator, etc. in the lithium secondary battery, an operation and an effect with the same said of ***** are acquired by ambient atmosphere systems other than argons, such as nitrogen, in the ambient atmosphere when generating a lithium fluoride film and a lithium-chloride film on the negative-electrode surface. Moreover, cylindrical, flat, a square shape, etc. can also take the configuration instead of a coin form.

[0036]

[Effect of the Invention] if it is alike and is based on this invention as explanation was given [above-mentioned], it not only can obtain often [the yield] and easily the negative electrode for lithium secondary batteries which is high capacity and was excellent in high charge-and-discharge effectiveness or keeping-proof, but high-capacity-izing of a rechargeable battery and an improvement of keeping-proof will be easily achieved by adoption of a configuration of having made this negative electrode for lithium secondary batteries provide. Therefore, offer of the portable power supply corresponding to lightweight[small /]-izing of the power supply accompanying miniaturization of portable electronic devices etc. is attained recently.

[Translation done.]